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Insight into the high-pressure CO_2 pre-treatment of sugarcane bagasse for a delivery of upgradable sugars

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ABSTRACT

This work provides an insight into sugarcane bagasse pre-treatment carried out with greener and more sustainable CO_2/H_2O system. Temperatures and residence times at a fixed initial CO_2 pressure were studied to verify their effects on pre-treatment efficiency with regard to the chemical composition of both water-soluble and water-insoluble fractions as well as to the susceptibility of the latter to enzymatic hydrolysis at high total solids. Also, trends in enzymatic hydrolysis were analysed in function of biomass crystallinity. This work provides an integrated approach in the analysis of upgradable sugars that are released as a result of pre-treatment and enzymatic hydrolysis. At optimal pre-treatment conditions, $17.2\,g\cdot L^{-1}$ sugars were released in the water-soluble fraction mainly as pentoses in monomeric and oligomeric forms. The enzymatic hydrolysis of solids produced at these pre-treatment conditions gave $76.8\,g\cdot L^{-1}$ glucose in the substrate hydrolysate. The overall sugar yield delivered in both pre-treatment and enzymatic hydrolysis was 73.9 mol%. These results were compared to the chemical effect of hydrothermal and/or physico-chemical effects of N_2-aided hydrothermal processes and showed that the greener processing of biomass pre-treatment with CO_2 is advantageous for the integrated valorisation of industrial residues and delivery of upgradable sugars within the biorefinery concept.

1. Introduction

Lignocellulosic biomass, such as forestry materials, grasses and agricultural residues (*e.g.* sugarcane bagasse), is one of the most promising renewable resources for the production of materials, chemicals and biofuels [1]. Aiming to convert lignocellulosic biomass into any of these products, a complex matrix of biopolymers including cellulose, hemicellulose and lignin must be disrupted into a stream of hexoses and pentoses, and valuable lignin derivatives. However, its successful implementation is hinged on the development of an efficient pre-treatment technique aiming at the production of sugars at affordable costs. To accomplish this aim, one of the key bottlenecks, which must addressed, is the recalcitrance of biomass. Recalcitrance refers to a structural resistance of plant cell walls to chemicals and enzymes that is conferred by ultrastructural, molecular and chemical properties [2]. Up to date, several pre-treatment techniques have been described to overcome this lignin-hemicellulose barrier prior to enzymatic action, and in some cases, to decrease the crystallinity of cellulose and its respective degree of polymerisation [3]. Unfortunately though, most of these pre-treatments are characterised by moderate selectivities and modest sugar yields, sometimes requiring overwhelming energy and/or chemical inputs [4]. These drawbacks, which often impose the economic viability of the entire process, have driven to the extensive development of new and advanced pre-treatment technologies [5]. One of them is the use of high-pressure CO_2/H_2O, in which the carbonic acid formed *in-situ* dissociates and leads to a progressive acidification of the reaction mixture. Consequently, the hydrolysis of hemicelluloses speeds up, especially over those found in hydrothermal pre-treatments where the initiator (carbonic acid) is absent, while leaving behind a cellulose-rich substrate that is more susceptible to enzymatic hydrolysis [6]. Furthermore, high-pressure CO_2/H_2O offers a possibility to produce a liquid stream without degradation products in

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